

CARBON ISOTOPES AS TRACERS OF BIOGENIC AND
FOSSIL FUEL DERIVED CARBON TRANSPORT IN THE ATMOSPHERE

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INTRODUCTION

Carbonaceous aerosols in the atmosphere are complex in nature and are derived from a variety of sources. Improved methods for characterization of organic and elemental fractions of these materials are urgently needed, especially to assess the contributions to carbonaceous aerosols from biogenic and anthropogenic sources of their gaseous and primary particulate precursors. As pointed out previously by several groups(1-5), carbon isotopes (^{13}C and ^{14}C) can be used to obtain new information on carbon source terms. The measurement of ^{14}C content by microscale gas proportional counting (6,7) or by direct ^{14}C atom counting with high energy nuclear accelerators (8) can provide direct evidence of the quantitative role of fossil fuel emissions (evaporation and combustion) vis-a-vis natural emissions from vegetation and human-derived emissions from biomass combustion with respect to the atmospheric carbon cycle.

The additional measurement of $^{13}\text{C}/^{12}\text{C}$ ratios in carbonaceous aerosols by isotope-ratio mass spectrometry provides information concerning fractionation processes but also can distinguish between biomass combustion sources involving C-3 plants (slash burning of corn, sugar cane) and C-4 plants (wood-burning)(9). This paper discusses recent data acquired at BNL demonstrating the value of ^{14}C and ^{13}C measurements in source allocation of carbonaceous aerosol fractions in the atmosphere. We further discuss the potential application of these techniques for mixed-phase studies of organic oxidant formation of direct relevance to acidic deposition in non-urban and remote atmospheres.

EXPERIMENTAL

Organic/elemental carbon speciation is performed on μg -sized samples using a thermal evolution technique (10) in which carbon is evolved in 2 discrete steps at 4000°C in He and at 650°C in 10% O_2/He , then measured as CO_2 by NDIR spectroscopy. $^{13}\text{C}/^{12}\text{C}$ measurements are made by isotopic ratio mass spectrometry (Nuclide Corp) also after conversion to CO_2 ; ratios in samples of as little as 0.5 mg can be determined to $\pm 0.1\text{‰}$ units.

Carbon-14 content is measured by specially designed gas proportional counters (7). Aerosol samples are first converted to CO_2 by combustion in a macroscale version of the thermal evolution technique. A clam shell oven was used to heat the sample for sequential evolution of organic and elemental carbon under equivalent conditions. Due to the possibility of thermal gradients, conditions in the macroscale apparatus were adjusted to produce the same recoveries of total carbon ($\mu\text{g C per cm}^2$ of filter area) as for the microscale apparatus. Carbon-14 data are reported as $\%$ contemporary carbon. Aldehyde data referred to in this paper were obtained by impinger sampling in dinitrophenylhydrazine/acetonitrile solution and analysis of the derivatives by HPLC with UV detection (11). Olefin measurements were made by a specially designed

ozone-chemiluminescence apparatus (12); difficulties in calibration accuracy and background drift with temperature limit its use to inferences of relative reactive hydrocarbon levels.

RESULTS AND DISCUSSION

Summaries of the aerosol carbon data obtained as part of the POLLutant-TERPene Canopy Interaction Studies (Poltercaist I and II) conducted at the NOAA Atmospheric Turbulence and Diffusion Laboratory (ATDL) site near Oak Ridge, TN in cooperation with NOAA-ATDL and Oak Ridge National Laboratory (ORNL) staff are reported in Tables 1 and 2. Table 1 concentrates on the organic and elemental carbon data obtained at the Oak Ridge site. Compared to previously reported data (5) from urban and rural sites in the N.E. USA and from Barrow, AK in winter Arctic haze episodes, concentrations of both organic and especially elemental carbon were quite high. Organic/total C (total = organic + elemental C) ratios were quite low and suggest the presence of substantial local sources of aerosol carbon in both summer and late winter seasons.

Some significant differences in measured organic/total C ratios by macro- and microscale techniques were observed, with the macroscale apparatus yielding higher ratios. This suggests that improvement in the macroscale technique to better simulate the rapid, uniform heating of the microscale apparatus is in order. However, differences were not large enough to affect the conclusion that local sources, possibly due to incineration, make dominant contributions to local aerosol carbon levels, and that levels of aerosol carbon make a non-trivial contribution to aerosol loadings and concomitant visibility effects. This contrasts with the summertime results in the nearby Great Smoky Mountains (13) in which aerosol carbon effects on visibility were much smaller than those produced by aerosol sulfate levels. Summertime levels of aerosol sulfate were comparably high in both studies.

Table 2 presents the data for $^{13}\text{C}/^{12}\text{C}$ ratios and ^{14}C content of aerosols collected at the ATDL/Oak Ridge site. The ^{14}C results for two samples in which both organic and element ^{14}C carbon were measured on the same sample are in agreement with predictions that elemental carbon (soot) in atmospheric aerosols is due to primary emissions from combustion of fossil fuels to a greater extent than is organic carbon in aerosols, leading to lower ^{14}C content. The organic carbon may come from a large range of biomass materials of recent origin (leaf litter, carbon in resuspended soil, pollen, etc.) as well as primary and secondary combustion aerosols. In contrast, all soot must come from combustion sources and, although wood combustion makes a major impact on aerosol elemental carbon in some locations especially in winter (3), most elemental carbon is thought to be derived from fossil fuel burning. The high levels of contemporary elemental carbon samples even in the summer season strongly suggests that there are local soot sources from combustion of contemporary carbon-containing fuels other than wood.

In addition to aerosol measurements within and above the canopy during Poltercaist I and II studies, reactive trace gases (HNO_3 , O_3 , NO_x , olefins, reduced sulfur compounds and aldehydes) were also measured (14). In summer, 1983, increased levels of olefins (~ 2-fold) sampled after a significant rainfall were accompanied by increases in formaldehyde (HCHO) levels but not of acetaldehyde (CH_3CHO) levels. Isoprene emissions from the deciduous forest canopy are deduced to be the cause of increased HCHO levels, indicating biogenic contributions to gas phase organic oxidant precursors, but not directly to organic aerosol carbon formation. Much lower ratios of $\text{HCHO}/\text{CH}_3\text{CHO}$ were observed during winter, 1984, sampling when the deciduous canopy was dormant. Additional measurements are required in coniferous forest canopies in which emissions are different in nature (terpenes vs. isoprene) and emitted in a more

Table 1

POLTERCAIST I and II
Organic/Elemental Carbon
Oak Ridge, TN; July, 1983 and March, 1984

Sample	Sampling Time	Sample Wt., mg	Microanalysis			Macroanalysis Org/Total C
			Org C µg/m ³	Elem C µg/m ³	Org/ Total	
I:C-1 (Org)	1937, 7/14 to 2005, 7/15	$\left\{ \begin{array}{c} 7.5 \\ 6.2 \end{array} \right\}$	5.26	5.32	0.50	0.55
I:C-1 (Elem)						
I:C-2 (Elem)	2015, 7/15 to 0843, 7/18	10.2*	3.52	4.63	0.43	NA
I:C-4 (Total)**	1105, 7/20 to ?	7.1	3.59	4.25	0.46	0.75
I:C-5 (Total)	1008, 7/21 to 0852, 7/22	11.4	5.02	4.42	0.53	0.62
II:C-1 (Total)	2050, 3/8/84 to 0939, 3/10	10.1	3.30	7.2	0.31	0.54
II:C-2 (Org)	0940, 3/10 to 1356, 3/12	6.5	5.9	6.2	0.49	0.59
II:C-3,4 (Org)	1357, 3/12 to 0933, 3/16	$\left\{ \begin{array}{c} 14.1 \\ 7.4 \end{array} \right\}$	8.3	4.7	0.64	0.66
II:C-3,4 (Elem)						

* Weight of elemental fraction only, organic fraction lost.

** Total samples are weight-averaged for elemental and organic carbon content.

Table 2

POLTERCAIST I and II
Organic/Elemental Carbon, $^{13}\text{C}/^{12}\text{C}$ and ^{14}C Data
Oak Ridge, TN; July, 1983 and March, 1984

Sample	Sample Wt., mg	Microanalysis Org/Total ⁺	Macroanalysis Org/Total ⁺	$^{13}\text{C}/^{12}\text{C}$, δ	^{14}C , % Contemporary*
I:C-1 (Org)	7.5	0.50	0.55	{ -25.5	74
I:C-1 (Elem)	6.2				47
I:C-2 (Elem)	10.2		NA		63
I:C-4 (Total)**	7.1	0.46	0.75	-25.2	99
I:C-5 (Total)	11.4	0.53	0.62	-25.4	78
II:C-1 (Total)	10.1	0.31	0.54	-24.3	48
II:C-2 (Org)	6.5	0.49	0.59	-24.7	75
II:C-3,4 (Org)	14.1	0.64	0.66	{ -25.2	76
II:C-3,4 (Elem)	7.4	0.56			53

⁺ Org/Total = organic carbon/(organic + elemental carbon).

* Corrected to 1978 standard.

** Total samples are weight-averaged for elemental and organic carbon contents.

continuous pattern (15). For both types of canopy studies new isotopic ratio-based techniques are required, especially ^{14}C -measurements of ultra-high volume samples of gaseous species such as formaldehyde and, ultimately, of organic oxidants (PANs, ROOHs) and weak acids in atmospheric water samples, in order to trace the biogenic or anthropogenic origin of oxidized organics and other sinks from the atmosphere.

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